

# Fluctuating thermodynamics of active Brownian particles

Chandrima Ganguly<sup>1</sup> and Debasish Chaudhuri<sup>1,\*</sup>

<sup>1</sup>Indian Institute of Technology Hyderabad, Yeddumailaram 502205, Andhra Pradesh, India

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Examples of self propulsion in strongly fluctuating environment is abound in nature, e.g., molecular motors and pumps operating in living cells. Starting from Langevin equation of motion, we develop a fluctuating thermodynamic description of self propelled particles using simple models of velocity dependent forces. We derive fluctuation theorems for entropy production and a modified fluctuation dissipation relation, characterizing the linear response at non-equilibrium steady states. We study these notions in a simple model of molecular motors, and in the Rayleigh-Helmholtz and energy-depot model of self propelled particles.

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## I. INTRODUCTION

Living systems are by definition open and active, staying away from equilibrium by consuming and subsequently dissipating energy, thereby generating forces and motion. Subcellular components, e.g., motor proteins, cytoskeletal filaments etc. operate in a noisy environment, where fluctuations arise from thermal motion and, in many cases, chemical reactions [1]. In contrast to conventional Brownian motion where the forces acting on a particle are entirely due to external sources, the *active* Brownian particles can generate their own forces [2] utilizing chemical energies [1].

Traditional thermodynamic description in terms of average quantities does not provide satisfactory description of small assembly of colloidal particles, or nano-materials due to the presence of strong thermal fluctuations. In the last two decades, a theoretical framework has emerged that allows several exact relations for distributions of fluctuating quantities like work, heat and entropy characterizing individual trajectories of the particles [3–13]. At non-equilibrium steady states (NESS) entropy  $\sigma$  is continually produced, with its probability distribution obeying [12–14]

$$\frac{P(\sigma)}{P(-\sigma)} = \exp(\sigma/k_B). \quad (1)$$

This is known as the detailed fluctuation theorem (DFT) and was first observed in simulations of sheared liquids [13] and later derived using chaotic [12] and stochastic dynamics [7, 10]. For asymptotic steady states the above relation is obeyed with  $\sigma = \Delta s_m$ ,  $\Delta s_m$  being the change in entropy of the medium alone. If one considers the stochastic change in system entropy  $\Delta s$  as well,  $\sigma = \Delta s_{tot} = \Delta s + \Delta s_m$  signifying the total entropy change, the DFT remains valid even for finite time measurements [14]. Further,  $\Delta s_{tot}$  obeys an integral fluctuation theorem  $\langle \exp(-\Delta s_{tot}/k_B) \rangle = 1$  where  $\langle \dots \rangle$  de-

notes non-equilibrium average over fluctuating trajectories. This is closely related to the Jarzynski equation, that expresses equilibrium free energy difference in terms of non-equilibrium work done [9, 11]. These fluctuation theorems were verified in experiments on colloids [15–17], and granular matter [18], and successfully used to find out the free energy landscape of RNA [19, 20]. Fluctuation theorems were also derived for the flashing ratchet [21, 22], and other detailed models of molecular motors and enzymes [23]. However, given the complexity of living systems it may not always be possible to identify and model all the chemical processes and mechanochemical coupling responsible for autonomous force generation. Recently, the DFT was applied to measure the torque generation by a rotary motor  $F_1$  ATPase from its fluctuating trajectory [24]. This idea may be extended to other types of molecular motors to measure autonomous force or torque generation from their stochastic trajectories [25].

Response in equilibrium states is characterized by the fluctuation-dissipation theorem (FDT), and the ratio of correlation and response is often interpreted as effective temperature of systems at NESS [26, 27]. Recent theoretical work derived several forms of modified fluctuation-dissipation relations (MFDR) characterizing linear response at NESS and established additive correction to FDT due to the presence of non-zero steady state currents [28–34], thus showing that phenomenological characterization of active processes by effective temperatures is not consistent. Some of the theoretical predictions were verified experimentally [35, 36].

In this paper, we use stochastic Langevin motion of self propelled particles (SPP) to develop fluctuating thermodynamics. We assume that the self-propulsion force is velocity dependent, however, the details of the propulsion mechanism is not specified to begin with. Using this assumption, we derive a general form of fluctuating thermodynamics of SPPs in terms of energy balance and fluctuation theorems involving entropy production. In particular, we identify the contributions in entropy production due to self-propulsion and its coupling to external drive. We also derive a modified fluctuation-dissipation relation characterizing the linear response at

\*Electronic address: debc@iith.ac.in

steady states of SPPs. Finally, we apply our theoretical development on some specific model systems: a simple model of molecular motors, and models utilizing velocity dependent forces as self propulsion mechanism, namely, the Rayleigh-Helmholtz model and the energy-depot model.

## II. LANGEVIN EQUATION AND THE LAWS OF THERMODYNAMICS

To develop the notions of fluctuating thermodynamics of SPP systems, let us focus on one dimension (1d), for simplicity. Simplest models of SPPs, like that the Rayleigh-Helmholtz model or the energy-depot model, use velocity dependent autonomous force  $F(v)$  to model self-propulsion. The Langevin equation for the motion of each particle evolving in the presence of a time dependent external force  $f(t)$  has the form

$$\begin{aligned}\dot{x} &= v \\ \dot{v} &= -\gamma v + \eta + F(v) - \frac{\partial U(x)}{\partial x} + f(t)\end{aligned}\quad (2)$$

where  $-\gamma v$  is viscous dissipation,  $\eta$  is Gaussian white noise characterized by  $\langle \eta(t) \rangle = 0$ ,  $\langle \eta(t)\eta(t') \rangle = 2D_0\delta(t-t')$  with  $D_0 = \gamma k_B T$ ,  $U(x)$  denotes conservative potential due to inter-particle interaction or external source. We use particle mass  $m = 1$ , unless otherwise specified.

### A. First law

Multiplying the above equation by velocity  $v$  and integrating over a small time interval  $\tau$  we obtain a first law equivalent for each particle [37]

$$\Delta E = \Delta Q + \Delta W + \Delta Q_m \quad (3)$$

where  $E = (1/2)v^2 + U(x)$  is the internal energy,  $\Delta Q = \int^\tau dt v \cdot (-\gamma v + \eta)$  is the energy flow from the heat bath,  $\Delta W = \int^\tau dt v \cdot f(t)$  is the work done on the particle, and  $\Delta Q_m = \int^\tau dt v \cdot F(v)$  is the amount of energy flow from the internal *motor* degrees of freedom of the SPP to mechanical motion. This last part is what differentiates an SPP from a usual Brownian particle. Adding these contributions over all the particles in a system leads to an equivalent of the first law of thermodynamics for the whole system. It is straightforward to extend this relation to higher dimensions.

### B. Fluctuation theorem: connection with second law

Consider the time evolution of the system from  $t = 0$  to  $\tau$  through a path defined by  $X = \{x(t), v(t), f(t)\}$ .

The probability of this path is given by

$$\mathcal{P}_+ = \mathcal{N} \exp \left[ -\frac{1}{4D_0} \int_0^\tau dt \left( \dot{v} - g(v) + \frac{\partial U}{\partial x} - f(t) \right)^2 \right] \quad (4)$$

where  $\mathcal{N}$  is the normalization constant, and we used  $g(v) = -\gamma v + F(v)$  to bring together all the velocity dependent forces in Langevin equation. Reversing the velocities gives us the time reversed path  $X^\dagger = \{x'(t'), v'(t'), f'(t')\} = \{x(\tau-t), -v(\tau-t), f(\tau-t)\}$ , the probability of which can be expressed as

$$\mathcal{P}_- = \mathcal{N} \exp \left[ -\frac{1}{4D_0} \int_0^\tau dt \left( \dot{v} + g(v) + \frac{\partial U}{\partial x} - f(t) \right)^2 \right] \quad (5)$$

where in the last step it was assumed that  $g(v)$  is an odd function  $g(-v) = -g(v)$ . This condition is naturally satisfied in many SPP models that assume energy transduction from internal energy source to kinetic energy [38], as will be illustrated further in the following sections. Thus the ratio of the probabilities of the forward and reverse paths comes out to be

$$\frac{\mathcal{P}_+}{\mathcal{P}_-} = \exp \left[ \frac{1}{D_0} \int_0^\tau dt \left( \dot{v} + \frac{\partial U}{\partial x} - f(t) \right) g(v) \right]$$

After some algebra one finally gets (see Appendix-A)

$$\frac{\mathcal{P}_+}{\mathcal{P}_-} = \exp \left[ -\beta \left( \Delta Q + \Delta Q_m + \Delta Q_{em} + \frac{1}{\gamma} \Delta \phi \right) \right] \quad (6)$$

where  $\beta = 1/k_B T = \gamma/D_0$ . In the above relation we have used  $\Delta Q$  and  $\Delta Q_m$  as identified in the derivation of the first law. The term  $\gamma \Delta Q_{em} = \int_0^\tau dt F(v) \cdot (f(t) - \partial_x U)$  is due to the coupling between the internal motor degrees of freedom and mechanical forces. This can be interpreted as an energy flow to motor from external forces and inter-particle interactions. In deriving the above relation  $F(v) = -\partial \phi(v)/\partial v$  was used, where  $\phi(v)$  is a velocity dependent potential due to the internal motor of SPPs.

Eq.(6) gives the ratio of the probabilities of forward and reverse paths, given that the forward evolution takes the system from some initial state  $i$  to some specific final state  $f$ . Assuming that the normalized probability distribution of these two states are  $\pi_i$  and  $\pi_f$  respectively, the ratio of the forward and the reverse process is

$$\begin{aligned}\frac{P_f(X)}{P_r(X^\dagger)} &= \frac{\pi_i \mathcal{P}_+}{\pi_f \mathcal{P}_-} = e^{\Delta s/k_B} e^{-\beta(\Delta Q + \Delta Q_m + \Delta Q_{em} + \frac{1}{\gamma} \Delta \phi)} \\ &= \exp[\Delta s_f/k_B]\end{aligned}\quad (7)$$

where we used the *fluctuating* entropy content corresponding to the distributions of initial and final *states* of the SPP system given by the relation  $s_{i,f} = -k_B \ln \pi_{i,f}$  [14], such that  $\pi_i/\pi_f = \exp(\Delta s/k_B)$ . The total entropy production in the forward process is

$$\begin{aligned}\Delta s_f &= \Delta s - \frac{1}{T} \left( \Delta Q + \Delta Q_m + \Delta Q_{em} + \frac{1}{\gamma} \Delta \phi \right) \\ &= \Delta s - \frac{1}{T} \left( \Delta E - \Delta W + \Delta Q_{em} + \frac{1}{\gamma} \Delta \phi \right),\end{aligned}\quad (8)$$

where in the last step we used the first law given by Eq.(3).

The main contribution of this paper is the identification of this total entropy production Eq.(8) which contains two new terms as compared to a system of traditional Brownian particles. These are the energy exchange between the motor's internal degrees of freedom and the external mechanical forces  $\Delta Q_{em}$ , and a change in the velocity dependent potential  $\Delta\phi$ . Both these contributions disappear once the motor activity of the self propelled particles is switched off. Note that both  $\Delta Q_{em}$  and  $\Delta\phi(v)$  are hidden from the perspective of the first law, but appears in the expression of the total entropy change. This is due to the intrinsic *open* nature of the system with respect to the self propulsion mechanism.

Eq.(7) implies the integral fluctuation theorem [7]

$$\begin{aligned}\langle e^{-\Delta s_f/k_B} \rangle &= \int \mathcal{D}[X] \frac{P_r(X^\dagger)}{P_f(X)} P_f(X) \\ &= \int \mathcal{D}[X^\dagger] P_r(X^\dagger) = 1.\end{aligned}\quad (9)$$

Using Eq.(8) for the total entropy production  $\Delta s_f$  in the forward process driven by a specific force protocol  $f(t)$  one can find a modified Jarzynski- type relation

$$\langle e^{-\beta\Delta W} \rangle = \langle e^{-\beta\Delta A} e^{-\beta(\Delta Q_{em} + \Delta\phi/\gamma)} \rangle \quad (10)$$

where  $\Delta A = \Delta E - T\Delta s$  would have been the canonical Helmholtz free energy difference if the initial and final states were at equilibrium. In the absence of motor driving,  $\Delta Q_{em} = 0$  and  $\Delta\phi = 0$ , the above relation leads to the Jarzynski equation  $\langle \exp(-\beta\Delta W) \rangle = \exp(-\beta\Delta A)$  [11].

Note that the total entropy production in the forward process  $\langle \Delta s_t \rangle = D(P_f||P_r) = \int \mathcal{D}[X] P_f(X) \ln(P_f/P_r)$  is the Kullback-Leibler distance between the probability distributions characterizing the forward and the reverse processes. Using Jensen inequality one obtains from Eq.(13)

$$\langle \Delta s_t \rangle = D(P_f||P_r) \geq 0, \quad (11)$$

i.e., any non-equilibrium process in SPP is associated with a maximization of the total non-equilibrium entropy  $S_t = \langle s_t \rangle$ . This notion should be contrasted against the equilibrium entropy maximization.

The principle of non-equilibrium entropy maximization is equivalent to the minimization of a non-equilibrium free energy like term  $\Delta G_m \leq 0$  where

$$G_m = [E - TS - W] + Q_{em} + \phi/\gamma \quad (12)$$

with  $S = \langle s \rangle$  denoting the average system entropy. In the absence of motor activity,  $Q_{em} = 0$ ,  $\phi = 0$  and  $G_m$  reduces to equilibrium Gibbs free energy  $G = E - TS - W$ .

### C. Fluctuating thermodynamics at NESS

It can be shown that at NESS the detailed fluctuation theorem (see Appendix-B)

$$\frac{\rho(\Delta s_t)}{\rho(-\Delta s_t)} = e^{\Delta s_t/k_B} \quad (13)$$

holds, where  $\Delta s_t$  is the total entropy change along any trajectory. In the absence of interaction  $U(x) = 0$ , the time evolution under a constant external force,

$$\dot{v} = -\gamma v + F(v) + f + \eta. \quad (14)$$

Writing  $g(v) = -\gamma v + F(v) + f \equiv -\partial\psi(v)/\partial v$ , the corresponding Fokker-Planck equation has the form

$$\partial_t p(v, t) = D_0 \partial_v \left[ e^{-\psi/D_0} \partial_v (e^{\psi/D_0} p) \right] \quad (15)$$

with a steady state solution

$$p_s(v) = \frac{1}{Z} e^{-\psi(v)/D_0} \quad (16)$$

where the normalization  $Z = \int_{-\infty}^{\infty} dv \exp(-\psi(v)/D_0)$ . Using  $F(v) = -\partial_v \phi(v)$  one obtains  $\psi(v) = (\gamma v^2/2 - f v) + \phi(v)$ . At NESS entropy is continually produced, and

$$\frac{\Delta s}{k_B} = \beta \left( \Delta E + \frac{\Delta\phi}{\gamma} - \frac{1}{\gamma} \Delta(f v) \right) \quad (17)$$

where  $E = v^2/2$  is the kinetic energy of the SPP. Therefore the corresponding change in the total entropy (Eq.8) is

$$\frac{\Delta s_t}{k_B} = \beta \left( -\frac{1}{\gamma} \Delta(f v) + \Delta W - \Delta Q_{em} \right). \quad (18)$$

This expression of  $\Delta s_t$  will obey the integral and the detailed fluctuation theorems derived in Eqs (9) and (13).

### III. LINEAR RESPONSE AT NESS: MODIFIED FLUCTUATION DISSIPATION RELATION

The Fokker-Planck equation corresponding to Eq.(2) is

$$\partial_t p(x, v, t) = \mathcal{L}(x, v, h) p(x, v, t) = (\mathcal{L}_0 + h(t) \mathcal{L}_1) p \quad (19)$$

where

$$\begin{aligned}\mathcal{L}_0 p &= -\partial_x(v p) - \partial_v [g(v) - \partial_x U] p + D_0 \partial_v^2 p \\ \mathcal{L}_1 p &= -\partial_v p.\end{aligned}$$

Here we replaced the external force  $f(t)$  by  $h(t)$  denoting a weak time dependent perturbation around the steady state. Assuming that the SPP system goes to a steady

state characterized by a distribution function  $p_s$  obeying  $\mathcal{L}_0 p_s = 0$ , linear response around this steady state is described by [34, 39]

$$\frac{\delta \langle A(t) \rangle}{\delta h(t')} = \langle A(t) M(t') \rangle_s \quad (20)$$

where  $\langle \dots \rangle_s$  indicate a steady state average, and  $M = (1/p_s) \mathcal{L}_1 p_s$ .

The steady state distribution of Eq.(16) leads to  $M = \partial_v [-\ln p_s] = \psi'(v)/D_0 = -g(v)/D_0 = (\gamma v - F(v))/D_0$ . Therefore the response function is given by

$$\begin{aligned} \frac{\delta \langle A(t) \rangle}{\delta h(t')} &= \frac{1}{D_0} \langle A(t) [\gamma v(t') - F(v(t'))] \rangle_s \\ &= \beta \langle A(t) v(t') \rangle - \frac{1}{D_0} \langle A(t) F(v(t')) \rangle. \end{aligned} \quad (21)$$

This is the modified fluctuation dissipation relation (MFDR) characterizing response function at NESS of SPP. In the absence of self propulsion,  $F(v) = 0$ , one gets back the equilibrium fluctuation dissipation theorem (FDT). The velocity response to external force is

$$\chi(t, t') = \frac{\delta \langle v(t) \rangle}{\delta h(t')} = \beta \langle v(t) v(t') \rangle - \frac{1}{D_0} \langle v(t) F(v(t')) \rangle \quad (22)$$

Since the correction in MFDR at NESS with respect to the equilibrium FDT is additive (see Eq. 22), not multiplicative, a ratio of the correlation and response  $\langle v(t) v(t') \rangle / \chi(t, t')$  can not, in general, be interpreted as an effective temperature, with the only possible exception being when  $F(v)$  is a linear function of velocity  $v$ .

In the following, we consider some specific models of self propelled particles and analyze their behavior using the formalism developed so far.

## IV. MODELS OF SPP

In this section we consider three specific models of SPP. The first one mimics the linear force-velocity relation of Kinesin like motor proteins [40]. The second model, known as the Rayleigh-Helmholtz model [38] has been useful to describe the collective motion of a bunch of motor proteins working in tandem to move appropriate cargo [41]. The third model is known as the energy-depot model [38, 42], which utilizes a simple coupling between internal energy production and mechanical motion as a self propulsion mechanism.

### A. Molecular motors

Molecular motors, e.g., kinesins move on polymeric tracks, e.g., microtubules in a highly stochastic but directed manner utilizing chemical energy from ATP hydrolysis. In the presence of load force acting in the direction opposing their motion, they slow down and eventually stop moving. This behavior can be approximately

modeled through a linear force-velocity relation [43]. Let us assume the autonomous force produced by the motor is a constant  $f_s$ . In the presence of an external load  $-\lambda$  acting opposite to the motor movement, the Langevin equation is

$$\dot{v} = -\gamma v + \eta + f_s - \lambda. \quad (23)$$

In the over-damped limit, this leads to the linear force-velocity relation  $\langle v \rangle = v_0(1 - \lambda/f_s)$  with  $v_0 = f_s/\gamma$  the autonomous velocity of free motors, and  $f_s$  the stall force. In molecular motors, the mechano-chemical processes leading to self propulsion, in general, may elevate the noise level, change the noise correlation, and change the viscous drag. However, in this simple model we assume that the noise can still be regarded as white if the time resolution is not too small, and the effective diffusion constant contains the impact of chemical reactions.

The Langevin equation can be rewritten as  $\dot{v} = -\psi'(v) + \eta$  where  $\psi'(v) = \gamma v - f_s$  is obtainable from  $\psi(v) = (\gamma/2)(v - v_0)^2$ . Thus the steady state distribution (see Eq.(16)) is a Gaussian peaked at  $v_0$

$$p_s(v) = \sqrt{\frac{\beta}{2\pi}} \exp\left(-\frac{\beta}{2}(v - v_0)^2\right). \quad (24)$$

#### 1. Entropy production at NESS

In calculating entropy, let us treat  $f_s$  similar to an external force. The total entropy production can be obtained from Eq.(18). In this case  $F(v) = 0 = \phi(v)$ , thus  $\Delta Q_{em} = 0$ . The total fluctuating entropy production

$$\frac{\Delta s_t}{k_B} = \beta \left[ -\frac{1}{\gamma} f_s \Delta v + \Delta W \right], \quad (25)$$

with  $\Delta W = f_s \int^\tau v dt$ . The integral and the detailed fluctuation theorems of Eqs (9) and (13) will be obeyed by this total entropy change at steady state.

One can extend this calculation to rotating motors, by replacing linear displacements by rotation, velocities by angular velocities, and forces by torques. Note that for measurements over asymptotically long time  $\tau$ ,  $\Delta W$  in the above expression becomes predominant and hence  $\Delta s_t/k_B = \beta \Delta W$  as has been used in recent experiments on F<sub>1</sub>ATPase [24].

#### 2. Entropy production at oscillatory steady states

In the presence of a time-dependent external force the Langevin equation describing the molecular motor is

$$\dot{v} = -\gamma v + \eta + f_s + f(t), \quad (26)$$

with the general solution at initial condition independent asymptotic states

$$v(t) = v_0 + \int_0^t dt' e^{-\gamma(t-t')} [f(t') + \eta(t')].$$

Thus  $v(t)$  is a linear functional of Gaussian noise  $\eta(t')$ , implying that the probability distribution of  $v(t)$  at this state is also Gaussian,

$$p(v, t) = \sqrt{\frac{\beta}{2\pi}} \exp\left(-\frac{\beta}{2}(v - \langle v(t) \rangle)^2\right) \quad (27)$$

where

$$\langle v(t) \rangle = v_0 + \int_0^t dt' e^{-\gamma(t-t')} f(t').$$

If the external force is sinusoidal  $f(t) = A \sin \omega t$ , the mean velocity at the asymptotic oscillatory state is

$$\langle v(t) \rangle = v_0 + \frac{A}{\gamma^2 + \omega^2} [\omega(1 - \cos \omega t) + \gamma \sin \omega t]. \quad (28)$$

The change in system entropy between any two times  $t_1$  and  $t_2$  is  $\Delta s/k_B = -\ln[p(v_2, t_2)/p(v_1, t_1)]$  and can be expressed as

$$\Delta s/k_B = \beta(\bar{v} - \langle \bar{v} \rangle)(\Delta v - \Delta \langle v \rangle) \quad (29)$$

with  $\bar{v} = (v_2 + v_1)/2$  and  $\Delta v = v_2 - v_1$ . Thus the integral fluctuation theorem of Eq.(9) is obeyed by the total entropy production between any two asymptotic non-equilibrium oscillatory states

$$\frac{\Delta s_t}{k_B} = \beta[\Delta W - \langle \bar{v} \rangle \Delta v - (\bar{v} - \langle \bar{v} \rangle) \Delta \langle v \rangle]. \quad (30)$$

### 3. Linear response at NESS

It is straightforward to obtain the velocity response to a perturbing force around a steady state of free molecular motors using Eq.(22)

$$k_B T \frac{\delta \langle v(t) \rangle}{\delta h(t')} = \langle v(t)v(t') \rangle_s - v_0^2. \quad (31)$$

Using the Langevin equation, one can directly calculate the two-time correlation function

$$\langle v(t)v(t') \rangle_s = v_0^2 + k_B T e^{-\gamma|t-t'|}. \quad (32)$$

Thus one obtains an equilibrium-like response

$$\frac{\delta \langle v(t) \rangle}{\delta h(t')} = e^{-\gamma|t-t'|}. \quad (33)$$

The 1d motion of molecular motors considered here is same as Brownian motion in presence of an external force. In higher dimensions, constant self propulsion  $f_s$  along with a steering of the direction of motion contrasts the properties of such SPPs from traditional Brownian motion under external field [38]. In 1d, such steering is equivalent to switching the direction of motion from forward to backward. This is achieved in the following examples by using velocity dependent self propulsion forces.

## B. The Rayleigh-Helmholtz model

In the Rayleigh-Helmholtz model [44] one assumes a velocity dependent potential  $\phi(v) = -(a/2)v^2 + (b/4)v^4$  so that the self propulsion force  $F(v) = -\phi'(v)$ . This force is often interpreted in terms of a non-linear velocity dependent friction  $\gamma_1(v)$  such that  $F(v) = -\gamma_1(v)v$  with  $\gamma_1(v) = -a + bv^2$  where  $-a$  acts like a negative friction.

This model in the deterministic limit has two fixed points at  $v = \pm \sqrt{a/b}$ . In presence of stochastic noise, thus, the velocity can switch between positive and negative directions. In the presence of a positive friction  $\gamma$ , for  $a > \gamma$  this model generates an effective negative friction  $\gamma' = \gamma - a$ , and pumps energy into the SPP. This model has recently been used in various studies of SPPs [38, 45–47], and describes the bimodal velocity distribution of microtubules under the collective influence of a set of bidirectional motor proteins NK11 [41].

### 1. Entropy production at NESS

In the presence of an external force  $\lambda$  all the forces can be clubbed together as  $-\psi'(v) = -\gamma v + F(v) + \lambda$  leading to  $\psi(v) = (\gamma/2)v^2 + \phi(v) - \lambda v = (\gamma/2)v^2 - (a/2)(v - v_\lambda)^2 + (b/4)v^4$  with  $v_\lambda = (\lambda/a)$ . Therefore, using Eq.(16) we find the steady state distribution

$$p_s(v, \lambda) = \frac{1}{Z} \exp \left[ -\beta \left( \frac{v^2}{2} - \frac{\alpha}{2}(v - v_\lambda)^2 + \frac{\nu}{4}v^4 \right) \right]. \quad (34)$$

where  $\alpha = a/\gamma$  and  $\nu = b/\gamma$  quantifies the amount of pumping. The corresponding fluctuating entropy content is  $s = -k_B \ln p_s$ . Within this model, the steady state has zero current in absence of external force  $\lambda$  which keeps the system out of equilibrium.

It is straightforward to use Eq.(18) to obtain the total entropy production between two microstates within a NESS. In a transformation from an initial state  $p_s(v_i, \lambda)$  to a final state  $p_s(v_f, \lambda)$ ,

$$\frac{\Delta s_t}{k_B} = \beta \left[ -\alpha v_\lambda \left( v_f - \frac{v_\lambda}{2} \right) + \Delta W - \Delta Q_{em} \right] \quad (35)$$

where the work done  $\Delta W = \lambda \int^\tau v dt$ , and  $\Delta Q_{em} = (\lambda/\gamma) \int^\tau dt F(v) = \alpha \Delta W - \nu \Delta W_0$ ,  $\nu \Delta W_0 = \nu \int^\tau v^3 dt$  having the dimension of energy. Thus we have

$$\frac{\Delta s_t}{k_B} = \beta \left[ -\alpha v_\lambda \left( v_f - \frac{v_\lambda}{2} \right) - (\alpha - 1) \Delta W + \Delta W_0 \right]. \quad (36)$$

This  $\Delta s_t$  obeys the integral and detailed fluctuation theorems described by Eq.s (9) and (13).

## 2. Linear response at NESS

The modified fluctuation dissipation relation, in this case, has the form

$$\begin{aligned}\chi(t, t') &= \beta \langle v(t)v(t') \rangle_s - \frac{1}{D_0} \langle v(t)[av(t') - bv^3(t')] \rangle_s \\ &= -\beta(\alpha - 1) \langle v(t)v(t') \rangle_s + \beta\nu \langle v(t)v^3(t') \rangle_s\end{aligned}\quad (37)$$

where  $\langle \dots \rangle_s$  is the steady state average in the absence of external force. Note that at equilibrium  $\alpha = 0 = \nu$ , and we get  $k_B T$  as the fluctuation dissipation ratio. However, in general this ratio  $\langle v(t)v(t') \rangle / \chi(t, t')$  depends on higher order correlation. Thus the effective temperature defined as a fluctuation-response ratio does not characterize the NESS.

## 3. Entropy production: external harmonic trap

If a free SPP of the Rayleigh-Helmholtz type is subjected to an external harmonic trap potential  $\frac{1}{2}kx^2$ , the initial steady state described by Eq.(34) undergoes transformation to a final steady state achieved in the trapping potential. The Langevin equation describing the dynamics of the SPP in trap is,

$$\dot{v} = -\gamma(v)v - kx + \eta(t) \quad (38)$$

so that  $\gamma(v) = \gamma - a + bv^2$ . By multiplying the above equation with  $\dot{v}$  we get a Langevin equation for the time evolution of the Hamiltonian

$$\frac{dH}{dt} = -\gamma(v)v^2 + \eta(t).v \quad (39)$$

where  $H = v^2/2 + kx^2/2$ . In the deterministic limit of  $\eta = 0$ , the motion goes to fixed points governed by  $\gamma(v) = 0$  at  $v = \pm v_0$  with  $v_0 = \sqrt{(a - \gamma)/b}$ . The dynamics is then characterized by  $x = x_0 \sin(\omega t + \phi)$ ,  $v = v_0 \cos(\omega t + \phi)$  with  $\omega^2 = k$  and  $x_0 = v_0/\omega$ . The corresponding energy near the fixed points  $H \simeq H_0 = v_0^2$ .

The stochastic dynamics near these fixed points is governed by the following Langevin equation obeyed by the Hamiltonian [48]

$$\frac{dH}{dt} = -\gamma_H H + \sqrt{H}\eta \quad (40)$$

where  $\gamma_H = \gamma - a + bH$ . The corresponding Fokker-Planck equation

$$\frac{\partial P_H(H, t)}{\partial t} = \frac{\partial}{\partial H} \left[ (\gamma_H H - D_0)P_H + D_0 \frac{\partial}{\partial H} (H P_H) \right] \quad (41)$$

has the steady state solution

$$p_s(H) = \mathcal{A} \exp \left[ -\frac{1}{D_0} \int \gamma_H dH \right]. \quad (42)$$

The most probable energy is given by the fixed point  $H = \frac{1}{2}v^2 + \frac{1}{2}kx^2 = H_0$  where  $\gamma_H(H_0) = 0$ . Thus near  $H = H_0$  we can expand  $\gamma_H$  as

$$\gamma_H = b(H - H_0) \quad (43)$$

to obtain

$$p_s(H) = \mathcal{A} \exp \left[ -\frac{b}{2D_0} (H - H_0)^2 \right]. \quad (44)$$

Thus in this case the steady state probability distribution is

$$\begin{aligned}\tilde{p}_s(x, v) &= \mathcal{N} e^{-\frac{\beta\nu}{2} \left( \frac{v^4}{4} - H_0 v^2 \right)} \\ &e^{-\frac{\beta\nu}{2} \left( \frac{1}{4} \omega^4 x^4 - H_0 \omega^2 x^2 \right)} e^{-\frac{\beta\nu}{2} \omega^2 x^2 v^2}.\end{aligned}\quad (45)$$

The most interesting part of this distribution is the term  $\exp[-(\beta\nu\omega^2/2)x^2v^2]$  which denotes that the particles with higher kinetic energies tend to locate near the central region of minimal potential, and the less mobile particles stays near the periphery.

We can now determine the change in steady state entropy as the initial steady state characterized by  $p_s(v_i, 0)$  (Eq.34) is transformed to  $\tilde{p}_s(x, v_f)$  given by Eq.(45). The change in system entropy is  $\Delta s/k_B = -\ln[\tilde{p}_s(x, v_f)/p_s(v_i, 0)]$  and can be expressed as

$$\begin{aligned}\frac{\Delta s}{k_B} &= \beta \left( \Delta E + \frac{\Delta \phi}{\gamma} \right) + \frac{\beta}{2} \left[ -\frac{\nu}{4} (v_f^4 + \omega^4 x^4) \right. \\ &\quad \left. - (\alpha - 1)\omega^2 x^2 + \nu\omega^2 x^2 v_f^2 \right].\end{aligned}\quad (46)$$

The total entropy production in a trajectory (Eq.8),

$$\begin{aligned}\frac{\Delta s_t}{k_B} &= \frac{\beta}{2} \left[ -\frac{\nu}{4} (v_f^4 + \omega^4 x^4) - (\alpha - 1)\omega^2 x^2 + \nu\omega^2 x^2 v_f^2 \right] \\ &\quad - \beta[(\alpha - 1)\Delta W - \nu\Delta W_0]\end{aligned}\quad (47)$$

follows the integral and detailed fluctuation theorems given by Eqs (9) and (13).

## C. The energy depot model

Within the energy depot model [42], an SPP is capable of taking up external energy and store it in the internal energy depot, then transducing the energy into kinetic energy. A part of the stored energy is dissipated during conversion into kinetic energy. Thus the energy balance equation for an internal energy  $e(t)$  can be given by,

$$\frac{de(t)}{dt} = q(\mathbf{r}) - ce(t) - h(\mathbf{v})e(t) \quad (48)$$

where  $q(\mathbf{r})$  is the space dependent rate of energy uptake, and  $h(\mathbf{v})$  is the rate of conversion of internal energy to kinetic energy. In a particular simple version of the model, one makes the choice  $q(\mathbf{r}) = q_0$ , i.e., uniform energy uptake and  $h(\mathbf{v}) = d\mathbf{v}^2$ , conversion rate proportional to the

kinetic energy itself. The corresponding Langevin equation in 1d is written as,

$$\begin{aligned}\dot{x} &= v \\ \dot{v} &= -\gamma v + \eta(t) + ae(t)v + \lambda\end{aligned}\quad (49)$$

where  $\lambda$  is an external force. Assuming that the kinematics of internal energy is much faster than diffusion, one replaces  $e(t)$  by the steady state energy  $e_0 = \frac{q_0}{c+dv^2}$ . Then the self propulsion force is given by,

$$F(v) = ae_0v = \frac{aq_0v}{c+dv^2}. \quad (50)$$

In the limit of small velocities this model reduces to the Rayleigh-Helmholtz model  $F(v) = \gamma_1v - \gamma_2v^3$  where  $\gamma_1 = aq_0/c$  and  $\gamma_2 = aq_0d/c^2$ .

All the forces in the Langevin equation can be clubbed together to  $-\psi'(v) = -\gamma v + \lambda + aq_0v/(c+dv^2)$  leading to  $\psi(v) = \frac{1}{2}\gamma v^2 - \lambda v + \phi(v)$  with the velocity dependent potential

$$\phi(v) = -\frac{aq_0}{2d} \ln(c+dv^2). \quad (51)$$

Thus using Eq.16, the steady state distribution is

$$p_s(\lambda, v) = \frac{1}{Z} (c+dv^2)^{aq_0/2D_0d} e^{-\frac{\beta}{2}v^2 + \frac{\lambda v}{D_0}}. \quad (52)$$

The steady state entropy production due to a transformation from initial state  $p_s(\lambda, v_i)$  to a final state  $p_s(\lambda, v_f)$  is obtainable from Eq.18, with  $\Delta W = \lambda \int^\tau dtv$ ,  $\Delta(fv) = \lambda(v_f - v_i)$  and  $\Delta Q_{em} = (\lambda/\gamma) \int^\tau dtv/(c+dv^2)$ . This entropy production at NESS will obey the integral as well as the detailed fluctuation theorems.

The linear response around  $\lambda = 0$  steady state can be expressed in terms of the modified fluctuation dissipation relation Eq.(22) with  $F(v)$  given by Eq.(50), such that

$$\chi(t, t') = \beta \langle v(t)v(t') \rangle - \frac{aq_0}{D_0} \left\langle v(t) \frac{v(t')}{c+dv^2(t')} \right\rangle. \quad (53)$$

## V. CONCLUSION

We have presented a fluctuating thermodynamic description of self propelled particles. This enabled us to identify a production of fluctuating entropy associated with non-equilibrium processes in SPP. We have shown that the trajectory averaged entropy gets maximized in non-equilibrium processes, playing a role similar to that of thermodynamic entropy in equilibrium irreversible processes.

For a simple model of molecular motors, we utilized this description to calculate the total fluctuating entropy production. This has been done for two cases: (i) at non-equilibrium steady state, (ii) transformation between oscillatory non-equilibrium states. We further studied entropy production in a model of non-linear velocity-dependent friction, namely, the Rayleigh-Helmholtz model, and in the energy-depot model of self

propelled particles. Our calculations show that the velocity dependent potential as a mechanism of self propulsion leads to associated excess entropy production, which is absent in traditional Brownian motion driven out of equilibrium by external force. Calculation of entropy in SPPs has gained recent experimental interest in measurements of force generation by molecular motors using the detailed fluctuation theorem [24, 25].

Further, we have characterized the steady state response function in terms of a modified fluctuation-dissipation relation. This in general has an additive correction due to self propulsion, compared to the fluctuation-dissipation theorem at equilibrium. Due to the close relation between the Rayleigh-Helmholtz model and the motion of microtubules under collective influence of a type of Ncd mutant NK11 [41, 49], our predictions on entropy production and fluctuation theorem in the context of Rayleigh-Helmholtz model are particularly amenable to experimental verification. We plan to extend the current formalism to SPPs moving in higher dimensions.

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## Appendix A: Ratio of probabilities

The ratio of the probabilities of the forward and reverse paths comes out to be

$$\begin{aligned}\frac{\mathcal{P}_+}{\mathcal{P}_-} &= \exp \left[ \frac{1}{D_0} \int_0^\tau dt \left( \dot{v} + \frac{\partial U}{\partial x} - f(t) \right) g(v) \right] \\ &= \exp \left[ \frac{1}{D_0} \int_0^\tau dt (-\gamma v + \eta + F(v)) (-\gamma v + F(v)) \right]\end{aligned}\quad (A1)$$

where in the last step we used the Langevin equation and the expression of  $g(v)$ . The terms in the exponential can be rewritten in the form

$$\begin{aligned}&\int_0^\tau dt (-\gamma v + \eta) (-\gamma v + F(v)) (F(v) - 2\gamma v + \eta) \\ &= -\gamma \Delta Q + \mathcal{I}\end{aligned}\quad (A2)$$

where the definition of  $\Delta Q$  is used from the first law Eq.(3), with the second term

$$\begin{aligned}\mathcal{I} &= \int_0^\tau dt F(v) [\dot{v} - \gamma v - (f(t) - \partial_x U)] \\ &= - \int_0^\tau dt \left[ \dot{v} \frac{\partial \phi}{\partial v} + \gamma v F(v) + F(v) \cdot (f(t) - \partial_x U) \right] \\ &= -\Delta \phi - \gamma \Delta Q_m - \gamma \Delta Q_{em}.\end{aligned}\quad (A3)$$

In the first term in the expression of  $\mathcal{I}$ , we have assumed  $F(v) = -\partial\phi(v)/\partial v$  and thus  $\int_0^\tau dt \dot{v} \cdot \partial_v \phi(v) = \phi(v(\tau)) - \phi(v(0)) = \Delta\phi$ , the change in velocity dependent potential. The second term  $\Delta Q_m = \int^\tau dt v \cdot F(v)$  is defined in the first law. In the third term we used the definition  $\gamma \Delta Q_{em} = \int^\tau dt F(v) \cdot (f(t) - \partial_x U)$ . Thus we get the ratio in Eq.(6).

## Appendix B: Detailed fluctuation theorem

It follows from Eq.(7) that the probability distribution of entropy production [7, 9]

$$\begin{aligned} \rho(\Delta s_t) &= \int \mathcal{D}[X] P_f(X) \delta(\Delta s_t - \Delta s_f(X)) \\ &= \int \mathcal{D}[X] P_r(X^\dagger) e^{\Delta s_f/k_B} \delta(\Delta s_t - \Delta s_f(X)) \\ &= e^{\Delta s_t/k_B} \int \mathcal{D}[X^\dagger] P_r(X^\dagger) \delta(\Delta s_t + \Delta s_r(X^\dagger)) \\ &= e^{\Delta s_t/k_B} \rho(-\Delta s_t) \end{aligned} \quad (\text{B1})$$

where we used  $\Delta s_f(X) = -\Delta s_r(X^\dagger)$ , i.e., the final distribution of the forward process is assumed to be the same as the initial distribution of the reverse process, and vice versa [9]. This assumption is valid at steady states, equilibrium or non-equilibrium.

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- [1] B. Alberts, D. Bray, K. Hopkin, A. Johnson, J. Lewis, M. Raff, K. Roberts, and P. Walter, *Essential Cell Biology*, 3rd ed. (Garland Science).
  - [2] T. Vicsek, ed., *fluctuations and scaling in biology* (Oxford, 2005).
  - [3] U. Seifert, Arxiv preprint arXiv:1205.4176 (2012), arXiv:arXiv:1205.4176v1 .
  - [4] C. Jarzynski, Annu. Rev. Condens. Matter Phys., **2**, 329 (2011).
  - [5] G. Hummer and A. Szabo, Proceedings of the National Academy of Sciences of the United States of America, **107**, 21441 (2010), ISSN 1091-6490.
  - [6] A. Saha, S. Lahiri, and A. Jayanavar, Physical Review E, **80**, 011117 (2009), arXiv:arXiv:0903.4147v2 .
  - [7] J. Kurchan, Journal of Statistical Mechanics: Theory and Experiment, **2007**, P07005 (2007), ISSN 1742-5468.
  - [8] O. Narayan and A. Dhar, J. Phys. A: Math. Gen., **37**, 63 (2004), arXiv:0307148v2 [arXiv:cond-mat] .
  - [9] G. Crooks, Physical Review E, **60**, 2721 (1999), arXiv:9901352v4 [arXiv:cond-mat] .
  - [10] J. Lebowitz and H. Spohn, Journal of Statistical Physics, **95**, 333 (1999).
  - [11] C. Jarzynski, Physical Review Letters, **78**, 2690 (1997), ISSN 0031-9007.
  - [12] G. Gallavotti and E. Cohen, Physical Review Letters, **74**, 2694 (1995).
  - [13] D. Evans, E. Cohen, and G. Morriss, Physical Review Letters, **71**, 2401 (1993).
  - [14] U. Seifert, Physical Review Letters, **95**, 040602 (2005), ISSN 0031-9007.
  - [15] G. Wang, E. Seivick, E. Mittag, D. Searles, and D. Evans, Physical Review Letters, **89**, 1 (2002), ISSN 0031-9007.
  - [16] V. Blickle, T. Speck, L. Helden, U. Seifert, and C. Bechinger, Physical Review Letters, **96**, 24 (2006), ISSN 0031-9007.
  - [17] T. Speck, V. Blickle, C. Bechinger, and U. Seifert, Euro. Phys. Lett., **79**, 30002 (2007), arXiv:arXiv:0705.0324v1 .
  - [18] S. Joubaud, D. Lohse, and D. van der Meer, Physical Review Letters, **108**, 210604 (2012), ISSN 0031-9007.
  - [19] J. Liphardt, S. Dumont, S. B. Smith, I. Tinoco, and C. Bustamante, Science (New York, N.Y.), **296**, 1832 (2002), ISSN 1095-9203.
  - [20] D. Collin, F. Ritort, C. Jarzynski, S. B. Smith, I. Tinoco, and C. Bustamante, Nature, **437**, 231 (2005), ISSN 1476-4687.
  - [21] D. Lacoste and K. Mallick, Biological Physics, **60**, 61 (2011), arXiv:arXiv:0912.0391v3 .
  - [22] D. Lacoste and K. Mallick, Phys. Rev. E, **80**, 021923 (2009), arXiv:arXiv:0907.1570v1 .
  - [23] U. Seifert, The European physical journal. E, Soft matter, **34**, 1 (2011), ISSN 1292-895X.
  - [24] K. Hayashi, H. Ueno, R. Iino, and H. Noji, Physical Review Letters, **104**, 218103 (2010), ISSN 0031-9007.
  - [25] K. Hayashi, M. Tanigawara, and J.-i. Kishikawa, Biophysics, **8**, 67 (2012), ISSN 1349-2942.
  - [26] N. Kikuchi, A. Ehrlicher, D. Koch, J. a. Käs, S. Ramaswamy, and M. Rao, Proceedings of the National Academy of Sciences of the United States of America, **106**, 19776 (2009), ISSN 1091-6490.
  - [27] S. Wang and P. Wolynes, PNAS, **108**, 15184 (2011).
  - [28] L. Cugliandolo, J. Kurchan, and G. Parisi, J. Phys. I France, **4**, 1641 (1994).
  - [29] T. Speck and U. Seifert, Europhysics Letters (EPL), **74**, 391 (2006), ISSN 0295-5075.
  - [30] M. Baiesi, C. Maes, and B. Wynants, Phys. Rev. Lett., **103**, 010602 (2009).



- [31] J. Prost, J.-F. Joanny, and J. Parrondo, *Physical Review Letters*, **103**, 1 (2009), ISSN 0031-9007.
- [32] U. Seifert and T. Speck, *EPL (Europhysics Letters)*, **89**, 10007 (2010), ISSN 0295-5075.
- [33] G. Verley, K. Mallick, and D. Lacoste, *EPL (Europhysics Letters)*, **93**, 10002 (2011), ISSN 0295-5075.
- [34] D. Chaudhuri and A. Chaudhuri, *Physical Review E*, **85**, 021102 (2012).
- [35] V. Blickle, T. Speck, C. Lutz, U. Seifert, and C. Bechinger, *Physical Review Letters*, **98**, 1 (2007), ISSN 0031-9007.
- [36] J. R. Gomez-Solano, A. Petrosyan, S. Ciliberto, R. Chetrite, and K. Gawedzki, *Phys. Rev. Lett.*, **103**, 040601 (2009).
- [37] K. Sekimoto, *Progress of Theoretical Physics Supplement*, **130**, 17c (1998).
- [38] P. Romanczuk, M. Bär, and W. Ebeling, *The European Physical Journal Special Topics*, **202**, 1 (2012).
- [39] G. S. Agarwal, *Zeitschrift für Physik*, **252**, 25 (1972), ISSN 1434-6001.
- [40] J. Howard, *Mechanics of Motor Proteins and the Cytoskeleton* (Sinauer Associates, 2001).
- [41] M. Badoual, F. Jülicher, and J. Prost, *Proceedings of the National Academy of Sciences of the United States of America*, **99**, 6696 (2002), ISSN 0027-8424.
- [42] F. Schweitzer, W. Ebeling, and B. Tilch, *Physical Review Letters*, **80**, 5044 (1998).
- [43] K. Svoboda and S. M. Block, *Cell*, **77**, 773 (1994), ISSN 0092-8674.
- [44] J. W. Rayleigh, *The Theory of Sound*, 2nd ed., Vol. 1 (Dover, New York, 1945).
- [45] U. Erdmann, W. Ebeling, and L. Schimansky-geier, *The European Physical Journal B*, **113**, 105 (2000).
- [46] J. Strefer, U. Erdmann, and L. Schimansky-Geier, *Physical Review E*, **78**, 1 (2008), ISSN 1539-3755.
- [47] B. Lindner, *New Journal of Physics*, **9**, 136 (2007).
- [48] L. Schimansky-Geier, *Acta Physica Polonica B*, **36**, 1757 (2005).
- [49] S. A. Endow and H. Higuchi, *Nature*, **406**, 913 (2000).